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TRANSMITTAL FORM

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Total Number of Pages in This Submission	35

Application Number	To Be Assigned
Filing Date	02/28/2006
First Named Inventor	RIVAS-NASS, Andreas et al.
Art Unit	To Be Assigned
Examiner Name	To Be Assigned
Attorney Docket Number	034166.021

ENCLOSURES *(check all that apply)*

- ☐ Fee Transmittal Form
  - ☐ Fee Attached
- ☐ Amendment / Reply
  - ☐ After Final
  - ☐ Affidavits/declaration(s)
- ☐ Extension of Time Request
- ☐ Express Abandonment Request
- ☐ Information Disclosure Statement
- ☐ Certified Copy of Priority Document(s)
- ☐ Reply to Missing Parts/ Incomplete Application
  - ☐ Reply to Missing Parts under 37 CFR1.52 or 1.53
- ☐ Drawing(s)
- ☐ Licensing-related Papers
- ☐ Petition
- ☐ Petition to Convert to a Provisional Application
- ☐ Power of Attorney, Revocation Change of Correspondence Address
- ☐ Terminal Disclaimer
- ☐ Request for Refund
- ☐ CD, Number of CD(s) ____
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- ☐ After Allowance Communication to TC
- ☐ Appeal Communication to Board of Appeals and Interferences
- ☐ Appeal Communication to TC **(Appeal Notice, Brief, Reply Brief)**
- ☐ Proprietary Information
- ☒ Status Letter
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Remarks

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm	Smith, Gambrell & Russell, LLP		
Signature			
Printed Name	Robert G. Weilacher		
Date	April 21, 2006	Reg. No.	20,531

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This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No.	: **To Be Assigned**	Confirmation No. **TBA**
Applicant(s)	: **RIVAS-NASS, Andreas et al.**	
Filed	: **February 28, 2006**	
TC/A.U.	: **To Be Assigned**	
Examiner	: **To Be Assigned**	
Title	: **Diene-Bis-Aquo-Rhodium(I) Complexes, Process for Preparing Them and Their Use**	

Docket No. : **034166.021**
Customer No. : **25461**

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Sir:

STATUS INQUIRY

Applicants ask to be informed of the status of the above-referenced patent application. Applicants are unaware of any action in this case since the date of mailing of the application by the Applicants. Applicants have not received their return receipt postcard, informally notifying the Applicants of the application serial number and filing date, nor have the Applicants received an Official Filing Receipt from the U.S. Patent and Trademark Office.

Applicants submit herewith a true and accurate copy of the following documents: Transmittal Letter to the U.S. Designated/Elected Office Concerning a Submission Under 35 U.S.C. 371, Preliminary Amendment, Information Disclosure Statement, return receipt postcard, and $1,250 check in payment of the filing fee, as submitted for filing to the U.S. Patent and Trademark Office on February 28, 2006. Applicants also submit a copy of Express Mail label EV462308455US, bearing the date-stamp of the U.S. Postal Service.

Respectfully submitted,

By: Robert G. Weilacher, Reg. No. 20,531

Dated: April 21, 2006
SMITH, GAMBRELL & RUSSELL, LLP
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Inventor(s): **RIVAS-NASS, Andreas et al.**
Serial No.: **To Be Assigned (National Phase of PCT/EP2004/008964)**
Filing Date: **Concurrently Herewith**
Title: **Diene-Bis-Aquo-Rhodium(I) Complexes, Process for Preparing Them and Their Use**

Papers Submitted:
1) **$1,250.00 Check;**
2) **Transmittal Letter to US DO/EO/US (3 pages);**
3) **Preliminary Amendment (6 pages);**
4) **Amendments to the Claims of PCT patent app.; and**
5) **Information Disclosure Statement and Form PTO/SB/08a with 1 cited foreign patent reference (16 pages)**

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TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A SUBMISSION UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	
034166.021	
U.S. APPLICATION NO. (If known, see 37 CFR 1.5) To Be Assigned	

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP2004/008964	10 August 2004 (10.08.2004)	28 August 2003 (28.08.2003)

TITLE OF INVENTION DIENE-BIS-AQUO-RHODIUM(I) COMPLEXES, PROCESS FOR PREPARING THEM AND THEIR USE

APPLICANT(S) FOR DO/EO/US RIVAS-NASS, Andreas et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a submission under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a submission under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☐ is attached hereto.
   b. ☒ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☒ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
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Items 11 to 20 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A preliminary amendment.
14. ☐ An Application Data Sheet under 37 CFR 1.76.
15. ☐ A substitute specification.
16. ☐ A power of attorney and/or change of address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 37 CFR 1.821- 1.825.
18. ☐ A second copy of the published International Application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
To Be Assigned	PCT/EP2004/008964	034166.021

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The following fees are submitted:	CALCULATIONS	PTO USE ONLY
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23. ☒ Search fee (37 CFR 1.492(b)) If the written opinion prepared by ISA/US to the international preliminary examination report prepared By IPEA/US indicates all claims satisfy provisions of PCT Article 33(1)-(4).....$0 Search fee (37 CFR 1.445(a)(2) has been paid on the international application to the USPTO as an International Searching Authority .....$100 International Search Report prepared by an ISA other than the US and provided in the Office or previously communicated to the US by the IB.....$400 All other situations $500	$ 500	
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CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	$
Total claims	25 - 20 =	5	x $50	$ 250
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MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $360	$

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NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.37(a) or (b)) must be filed and granted to restore the International Application to pending status.

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PATENT COOPERATION TREAT

From the INTERNATIONAL BUREAU

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Date of mailing *(day/month/year)* 07 July 2005 (07.07.2005)	
Applicant's or agent's file reference G5466 PCT	**IMPORTANT NOTICE**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP2004/008964	10 August 2004 (10.08.2004)	28 August 2003 (28.08.2003)

Applicant

UMICORE AG & CO. KG et al

The International Bureau transmits herewith the following documents:

☐ copy of the international application as published by the International Bureau on under No. WO

☑ copy of international application as republished by the International Bureau on 07 July 2005 (07.07.2005) under No. WO 2005/021153
For an explanation as to the reason for this republication of the international application, reference is made to INID codes (15), (48) or (88) (*as the case may be*) on the front page of the attached document.

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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 March 2005 (10.03.2005)

PCT

(10) International Publication Number
WO 2005/021153 A3

(51) International Patent Classification[7]: B01J 31/22, 37/30, C07F 15/00

(21) International Application Number: PCT/EP2004/008964

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(26) Publication Language: English

(30) Priority Data:
103 39 790.6 28 August 2003 (28.08.2003) DE

(71) Applicant (*for all designated States except US*): UMICORE AG & CO. KG [DE/DE]; Rodenbacher Chaussee 4, 63457 Hanau (DE).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): RIVAS-NASS, Andreas [DE/DE]; Am Hundacker 10, 55257 Budenheim (DE). PETER, Gerhard [DE/DE]; Jahnstrasse 11, 63579 Freigericht (DE). WIDMER, Jürgen [DE/DE]; Heidelberger Strasse 27a, 64285 Darmstadt (DE). BRIEL, Oliver [DE/DE]; Tulpenhofstrasse 25, 63067 Offenbach (DE). KARCH, Ralf [DE/DE]; Käthe-Kollwitz-Strasse 24, 63801 Kleinostheim (DE).

(74) Agent: VOSSIUS & PARTNER; Siebertstrasse 4, 81675 Munich (DE).

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— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations*

Published:
— *with international search report*
— *with amended claims*

(88) Date of publication of the international search report: 12 May 2005

Date of publication of the amended claims: 7 July 2005

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DIENE-BIS-AQUO-RHODIUM(I) COMPLEXES, PROCESS FOR PREPARING THEM AND THEIR USE

(57) Abstract: Diene-bis-aquo-rhodium(I) complex of the general formula $[Rh(diene)(H_2O)_2]X$ where diene is a cyclic diene and X is a noncoordinating anion.

WO 2005/021153 A3

AMENDED CLAIMS
[Received by the International Bureau on 17 May 2005 (17.05.2005)
Original claims 1-15 unchanged ; new claims 16-20 (3 pages)]

1. Diene-bis-aquo-rhodium(I) complex of the general formula (1):

$$[Rh(diene)(H_2O)_2]X \quad (1)$$

where diene is a cyclic diene and X is a noncoordinating anion.

2. Diene-bis-aquo-rhodium(I) complex according to Claim 1, wherein diene is 1,5-cyclooctadiene (COD) or norbornadiene (NBD).

3. Diene-bis-aquo-rhodium(I) complex according to Claim 1 or 2, wherein X is a noncoordinating anion selected from BF_4^- and $CF_3SO_3^-$.

4. Diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 3 having the name 1,5-cyclooctadienebisaquorhodium(I) tetrafluoroborate.

5. Diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 3 having the name 1,5-cyclooctadienebisaquorhodium(I) trifluoromethylsulphonate.

6. Diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 5, wherein the complex is in the form of a solid.

7. Process for preparing a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6, which comprises reacting a rhodium(I)-olefin compound with silver salts in an aqueous solvent mixture, characterized in that the silver salt is not added as a solid to the reaction mixture but is instead prepared in solution and added in this form.

8. Process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 7, wherein the silver salt is prepared in solution by reacting silver oxide (Ag_2O) with the acid corresponding to the noncoordinating anion of the diene-bis-aquo-rhodium(I) complex.

9. Process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 8 wherein the acid is used in an excess of up to 0.5 molar equivalents over the silver oxide.

10. Process for preparing a diene-bis-aquo-rhodium(I) complex according to any of Claims 7 to 9, wherein the preparation of the silver salt is carried out in an aqueous medium.

11. Process for preparing a diene-bis-aquo-rhodium(I) complex according to any of Claims 7 to 10, wherein the rhodium(I)-olefin compound is $[Rh(COD)Cl]_2$.

12. Process for preparing a diene-bis-aquo-rhodium(I) complex according to any of Claims 7 to 11, wherein the aqueous solvent mixture comprises water together with up to 10% by volume of at least one alcoholic solvent.

13. Process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 12, wherein the alcoholic solvent is selected from methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-butanol.

14. Use of a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6 in catalytic reactions.

15. Use of a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6 for preparing heterogeneous catalysts.

16. Use of a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6 for preparing a chirally nonselective, diastereoselective or enantioselective catalytically

active species.

17. Use according to Claim 16, wherein the diene-bis-aquo-rhodium(I) complex is reacted with achiral and/or chiral ligands with ligand exchange.

18. Use according to Claim 17, wherein the achiral and/or chiral ligands are selected from triphenylphosphine, ferrocenylphosphine, alkylphosphine or chiral phosphine.

19. Chirally nonselective, diastereoselective or enantioselective catalytically active species, obtainable by reacting a diene-bis-aquo-rhodium(I) complex according to any of Claims 1 to 6 with achiral and/or chiral ligands with ligand exchange.

20. Chirally nonselective, diastereoselective or enantioselective catalytically active species according to Claim 19, wherein the achiral and/or chiral ligands are selected from triphenylphosphine, ferrocenylphosphine, alkylphosphine or chiral phosphine.

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No.	**To Be Assigned (Nat'l Phase of PCT/EP2004/008964 filed 10/08/2004)**	Confirmation No.:
Applicant(s):	**ANDREAS RIVAS-NASS, ET AL.**	
Filed:	**Concurrently Herewith**	
TC/A.U.	**To Be Assigned**	
Examiner:	**To Be Assigned**	
Title:	**DIENE-BIX-AQUO-RHODIUM(I) COMPLEXES, PROCESS FOR PREPARING THEM AND THEIR USE**	
Docket No.:	**034166.021**	
Customer No.:	**25461**	

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PRELIMINARY AMENDMENT

Before the first examination, please amend the application as follows:

Amendments to the Claims are reflected in the listing of claims which begins on page 3 of this paper.

Remarks begin on page 6 of this paper.

CERTIFICATE OF MAILING

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Susan J. Revell

Amendments to the Claims:

This listing of claims will replace all prior versions, and listings of claims in the application:

Listing of Claims:

Please amend the claims as follows:

1-20 (Cancelled)

21. (New) Diene-bis-aquo-rhodium(I) complex of the formula:

$$[Rh(diene)(H_2O)_2]X \quad (1)$$

where diene is a cyclic diene and X is a noncoordinating anion.

22. (New) The diene-bis-aquo-rhodium(I) complex according to Claim 21, wherein diene is 1,5-cyclooctadiene (COD) or norbornadiene (NBD).

23. (New) The diene-bis-aquo-rhodium(I) complex according to Claim 21, wherein X is a noncoordinating anion selected from the group consisting of BF_4^- and $CF_3SO_3^-$.

24. (New) The diene-bis-aquo-rhodium(I) complex according to Claim 22, wherein X is a noncoordinating anion selected from the group consisting of BF_4^- and $CF_3SO_3^-$.

25. (New) The diene-bis-aquo-rhodium(I) complex according to Claim 21 having the name 1,5-cyclooctadienebisaquorhodium(I) tetrafluoroborate.

26. (New) The diene-bis-aquo-rhodium(I) complex according to Claim 22 having the name 1,5-cyclooctadienebisaquorhodium(I) tetrafluoroborate.

27. (New) Diene-bis-aquo-rhodium(I) complex according to Claim 21 having the name 1,5-cyclooctadienebisaquorhodium(I) trifluoromethylsulphonate.

28. (New) Diene-bis-aquo-rhodium(I) complex according to Claim 22 having the name 1,5-cyclooctadienebisaquorhodium(I) trifluoromethylsulphonate.

29. (New) The diene-bis-aquo-rhodium(I) complex according to Claim 21, wherein the complex is in the form of a solid.

30. (New) Process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 21, which comprises reacting a rhodium(I)-olefin compound with a silver salt in an aqueous solvent mixture as a reaction mixture, wherein the silver salt is prepared in solution and is added to the reaction mixture.

31. (New) The process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 30, wherein the silver salt is prepared in solution by reacting silver oxide (Ag_2O) with the acid corresponding to the noncoordinating anion of the diene-bis-aquo-rhodium(I) complex.

32. (New) The process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 30, wherein the acid is used in an excess of up to 0.5 molar equivalents over the silver oxide.

33. (New) The process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 30, wherein the preparation of the silver salt is carried out in an aqueous medium.

34. (New) The process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 31, wherein the preparation of the silver salt is carried out in an aqueous medium.

35. (New) The process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 30, wherein the rhodium(I)-olefin compound is $[Rh(COD)Cl]_2$.

36. (New) The process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 30, wherein the aqueous solvent mixture comprises water together with up to 10% by volume of at least one alcoholic solvent.

37. (New) The process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 31, wherein the aqueous solvent mixture comprises water together with up to 10% by volume of at least one alcoholic solvent.

38. (New) The process for preparing a diene-bis-aquo-rhodium(I) complex according to Claim 36, wherein the alcoholic solvent is selected from methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-butanol.

39. (New) In a catalytic reaction, the improvement comprising carrying out said reaction in the presence of diene-bis-aquo-rhodium(I) complex according to Claim 21.

40. (New) In a method for preparing a heterogeneous catalyst, the improvement comprising carrying out said method with presence of a diene-bis-aquo-rhodium(I) complex according to Claim 21.

41. (New) In a method for preparing a chirally nonselective, diastereoselective or enantioselective catalytically active species comprising carrying out said method in the presence of a diene-bis-aquo-rhodium(I) complex according to Claim 21.

42. (New) The method according to Claim 41, wherein the diene-bis-aquo-rhodium(I) complex is reacted with achiral and/or chiral ligands with ligand exchange.

43. (New) The method according to Claim 42, wherein the achiral and/or chiral ligands are selected from the group consisting of triphenylphosphine, ferrocenylphosphine, alkylphosphine and chiral phosphine.

44. (New) A chirally nonselective, diastereoselective or enantioselective catalytically active species, obtainable by reacting a diene-bis-aquo-rhodium(I) complex according to Claim 21 with achiral and/or chiral ligands with ligand exchange.

45. (New) The chirally nonselective, diastereoselective or enantioselective catalytically active species according to Claim 44, wherein the achiral and/or chiral ligands are selected from the group consisting of triphenylphosphine, ferrocenylphosphine, alkylphosphine and chiral phosphine.

REMARKS/ARGUMENTS

The amendments in the claims were presented to place the claims in U.S. format and to avoid charges for multi-dependent claims contained in the application.

These amendments are not related to reasons of patentability.

Examination on the merits is awaited.

Favorable action at the Examiner's earliest convenience is respectfully requested.

Respectfully submitted,

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No.	: **To Be Assigned**	Confirmation No. **TBA**
Applicant(s)	: **RIVAS-NASS, Andreas et al.**	
Filed	: **Concurrent Herewith**	
TC/A.U.	: **To Be Assigned**	
Examiner	: **To Be Assigned**	
Title	: **Diene-Bis-Aquo-Rhodium(I) Complexes, Process for Preparing Them and Their Use**	

Docket No.	: **034166.021**
Customer No.	: **25461**

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Sir:

INFORMATION DISCLOSURE STATEMENT

Pursuant to the duty of disclosure under 37 C.F.R. 1.56, Applicants are enclosing an Information Disclosure Statement by Applicant (Form PTO/SB/08a) and a copy of the foreign patent reference cited therein. The relevance of the cited documents is indicated in the International Search Report in the corresponding International Application No. PCT/EP2004/008964 mailed March 14, 2005, a copy of which is submitted herewith.

It is respectfully requested that the cited documents be considered by the Examiner in the above-identified patent application and that the cited documents be made officially of record therein. It is further requested that a listing of the same appear on the face of any patent which may issue from this application.

A first Official Action has not yet issued for this application. Therefore, it is believed that no fees are due under 37 C.F.R. Section 1.97(b)(3).

Respectfully submitted,

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Sheet 1 of 1

Complete if Known	
Application Number	To Be Assigned
Filing Date	Concurrent Herewith
First Named Inventor	RIVAS-NASS, Andreas et al.
Art Unit	To Be Assigned
Examiner Name	To Be Assigned
Attorney Docket Number	034166.021

U.S. PATENT DOCUMENTS

Examiner Initials *	Cite No.[1]	Document Number Number - Kind Code[2] (*if known*)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		US- 6,291,606	09-18-2001	TANG ET AL.	
		US-			
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FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Country Code[3] - Number[4] - Kind Code[5] (*if known*)	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T[6]
		WO 02/36261 A2	05-10-2002	IMPERIAL CHEMICAL INDUSTRIES PLC		✓

Examiner Signature		Date Considered	

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WO 02/36261 A2

(54) Title: CATALYST

(57) Abstract: A solid catalyst for asymmetric hydrogenation reactions is disclosed comprising a chiral cationic metal-ligand complex immobilised on a mesoporous alumino-silicate support. The catalyst is formed by ion exchange with the acid sites of the support. The catalyst is reusable, and maintains its activity after use.

Catalyst

The present invention concerns catalysts, especially catalysts which are useful for asymmetric reactions to produce chiral products. More specifically, the invention concerns immobilised chiral catalysts and processes that utilise such catalysts.

Asymmetric catalysis is increasingly important for the preparation of chiral products that are used in speciality applications such as in the manufacture of pharmaceuticals. Suitable catalysts for asymmetric reactions are well known in the art and include compounds containing chiral ligands such as DUPHOS™. Homogeneous catalysts are generally more advanced than their heterogeneous counterparts in this field, but there is considerable interest in the identification of heterogeneous asymmetric catalysts. The use of heterogeneous catalysts has several process advantages in facilitating product recovery, catalyst separation and reuse of the catalysts, which tend to be relatively expensive. In practice, however, the heterogenisation of homogenous catalysts has often led to a loss in catalytic activity and selectivity.

Three approaches in the design of heterogeneous catalysts may be considered. The first of these is the use of chiral support for an achiral metal catalyst. Secondly, the modification of an achiral heterogeneous catalyst using a chiral cofactor, for example nickel metal modified with tartaric acid and sodium bromide, which can be applied to the asymmetric hydrogenation of β-ketoesters and β-diketones; or platinum modified with a cinchona alkaloid which is useful for the enantioselective hydrogenation of α-keto esters and acids (see Blaser et al, *Catalysis Today 37 (1997) 441 – 463*). The third approach involves the immobilisation of a homogeneous chiral catalyst. The most common method in the prior art has been to attach a ligand or metal-ligand complex to a solid support material as described for example by Brandts et al *in 18th Conference on Catalysis of Organic Reactions Preprints Poster #4 (30 April – 4th May 2000)*. The reference describes tethering both chiral and non-chiral rhodium complexes to γ-alumina using an anchoring agent based on phosphotungstic acid, phosphomolydic acid or silicotungstic acid.

F. de Rege et al (*18th Conference on Catalysis of Organic Reactions Preprints Poster #4 (30 April – 4th May 2000; J. C. S. Chem. Comm., 2000, 1797 and Chem. Ind. 2001, 82, 439-450*) describe an immobilised chiral rhodium complex, [(R,R)-Me-(DuPHOS)-Rh(COD)][OTf]on silica-MCM-41. The complexes are anchored to the support by hydrogen bonding between the triflate anion of the complex and Si-OH groups on the silica surface. The resulting immobilised catalyst may be recovered from a reaction mixture and reused provided that a non-polar reaction solvent is used to avoid leaching of the active species.

Johnson et al (*Chem. Commun. 1999, 1167*) describe confining a chiral catalyst within the walls of a silica-MCM-41 by first deactivating the surface sites, then treating the internal walls with 3-bromopropyltrichlorosilane, reaction of the treated support with a precursor of the chiral catalyst, followed by further treatment to produce the final catalyst. The catalyst is thereby covalently linked to the chemically-modified silica support.

Hölderich in DE 19820411 describes hydrogenation catalysts prepared by mixing Al-MCM-41 with either (S,S)-MeDuPHOS and $[\{Rh(cod)Cl_2\}_2]$ or (R,R)-DIOP and $[Rh(acac)(CO)_2]$. In both cases the catalysts require long reaction times (at least 24 hours) and provide poor enantioselectivities compared to the homogeneous equivalents.

In order to overcome problems with the prior art systems, it is desirable to anchor a pre-formed homogeneous catalyst to a support, without the need for any ligand modification, or alternatively to anchor a suitable metal precursor to the support and then build the complex on the support by addition of a ligand. EP-A-0831086 describes the application of this technique to the enantioselective aziridination of alkenes using a Cu^{2+} - exchanged zeolite Y modified with bis(oxazolines). A similar approach has also been applied to the epoxidation of alkenes using a Manganese-exchanged Al-MCM-41 modified with chiral salen ligand (see Piaggio et al, *J.Chem Soc. Perkin Trans 2, 2000, 143*).

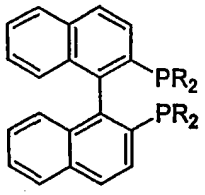
We have now found that cationic metal-ligand complexes may be immobilised using mesoporous alumino silicates and used to advantage in the asymmetric hydrogenation of prochiral alkenes.

According to the invention we provide a solid catalyst for asymmetric hydrogenation reactions comprising a chiral cationic metal-ligand complex immobilised on a mesoporous alumino-silicate support.

The chiral cationic metal-ligand complex may be any of those commonly used in the art of asymmetric hydrogenation in homogeneous form. Particularly suitable complexes comprises a cationic metal ion and a neutral mono- or bidentate ligand, which may be represented by the formula $[M(L)_n]^+$, in which;
M is a metal ion which may be selected from Rh^{1+}, Ir^{1+} or Ru^{2+},
L is a neutral mono- or bidentate ligand and n is 1 or 2.

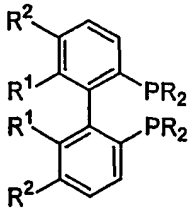
In addition to the neutral mono- or bidentate ligand the complex may further comprise at least one further stabilising ligand such as a diene, alkene, carbonyl or aryl group. 1,5-cyclooctadiene (cod) is the most preferred stabilising ligand for these systems.

The neutral mono- or bidentate ligands are selected from those containing P, N, O or S-donor atoms. Preferably, the ligands are bidentate and provide two donor atoms. Such ligands may be abbreviated to P-P, P-N, N-N, O-N and the like. Preferably the neutral ligands contain P donor atoms and most preferably the ligands are bidentate and chiral. Examples of suitable bidentate ligands are as follows:

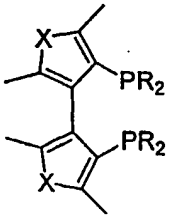


BINAP, R = aryl and alkyl

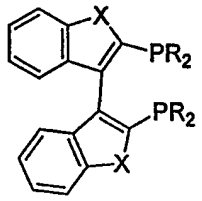
DUPHOS
R= alkyl, alkoxy, hydroxy, amino, aryl



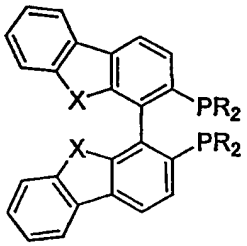
BIPHEP
R= aryl and alkyl
R^1= alkyl, alkoxy
R^2= H, alkyl, alkoxy



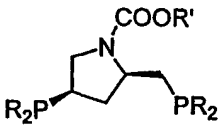
TMBTP
R= aryl, alkyl
X = O, S, N



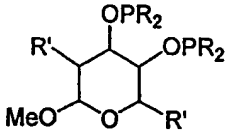
BITIANAP
R= aryl, alkyl
X = O, S, N



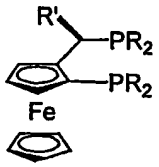
BIBFUP
R = aryl, alkyl
X = O, S, N



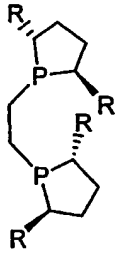
bppm
R = Aryl, Alkyl
R' = Alkyl



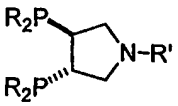
CARBOPHOS
R = aryl
R' = $CH_2C(O)Ph$



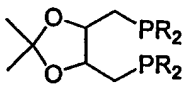
JOSIPHOS
R = alkyl, aryl
R' = alkyl, aryl



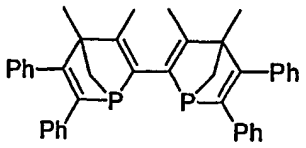
BPE
R = alky



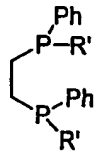
DEGPHOS
R = aryl
R' = H, Benzyl



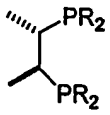
DIOP
R = aryl



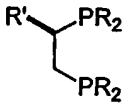
BIPNOR



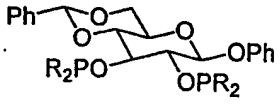
DIPAMP
R' = o-anisyl



CHIRAPHOS
R = aryl

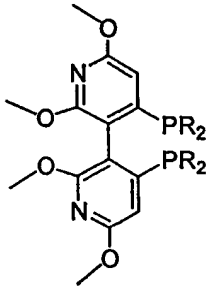


PROPHOS
R = aryl
R' = alkyl, aryl

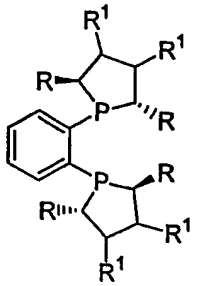


SELKE
R = Ph

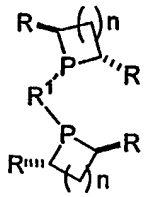
BINAPAN
R = aryl, alkyl



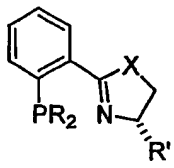
PYPHOS
R = aryl



R= H, alkyl, alkoxy, hydroxy, amino, aryl
R^1 = H, hydroxy, alkoxy, amino



R^1 = alkyl, aryl, ferrocenyl, ruthenocyl,
n = 0, 1, 2, 3 etc
R = alkyl, alkoxy, hydroxy, amino, aryl



R' = alkyl, phenyl,
R = aryl, alkyl, alkoxy, amino
X = O, S, N

Preferred chiral cationic metal-ligand complexes are rhodium(I) complexes of (R)-BINAP, (R)-PROPHOS, (R,R)-MeDuPHOS and (R,S)-JOSIPHOS and a particularly preferred complexes comprises [(R,R)-MeDuPHOS-Rh(I)(1,5-cyclooctadiene)]$^+$ and [(R,S)-JOSIPHOS)Rh(I)(1,5-cyclooctadiene)]$^+$.

The invention further provides a method of forming a solid catalyst comprising a chiral cationic metal-ligand complex immobilised on a mesoporous alumino-silicate support, comprising the steps of;

a) forming a solution of a metal-ligand complex $[M(L)_n]^+[X]^-$ where X is Cl, BF_4, OTf, or another suitable counter-ion in a polar solvent,

b) stirring together said solution with a solid support comprising a mesoporous aluminosilicate,

c) filtering the resulting solid from the supernatant liquor, and

d) washing the catalyst with solvent,

and a method of forming a solid catalyst comprising a chiral cationic metal-ligand complex immobilised on a mesoporous alumino-silicate support, comprising the steps of;

a) forming a solution of a cationic metal precursor in a polar solvent,

b) stirring together said solution with a solid support comprising a mesoporous aluminosilicate,

c) filtering the resulting solid from the supernatant liquor,

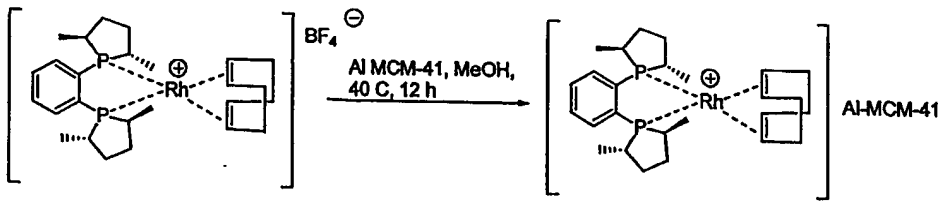
d) stirring together said solid with a solution of a neutral ligand in a solvent, and

e) filtering the resulting solid from the supernatant liquor.

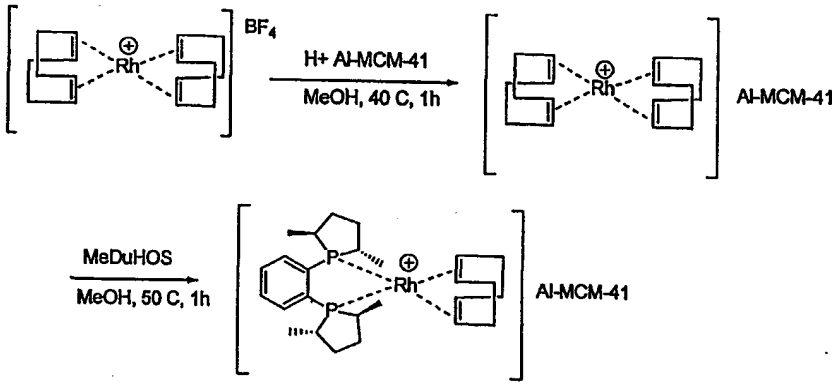
The immobilised catalysts are formed by ion-exchange between a cationic metal-ligand complex and the acidic protons of the mesoporous alumino silicate. The mesoporous alumino-silicate support is preferably a mesoporous silicate material having acidic sites which are suitable for ion exchange [(H^+)-alumino-silicate]. The presence of the aluminium provides acidic sites for ion exchange with the cationic metal-ligand complex. The Al content of the aluminosilicate is preferably selected to give a ratio of Si to Al of at least 4 and is preferably in the range 5 – 500 : 1 by weight. Preferred supports include SBA-15 and Al-MCM-41. SBA-15 is a hexagonal mesoporous silica with uniform pore size up to about 300 angstroms and is described by Zhao et al in *Science, 1998 (279), 548 – 552* and *J. Am. Chem. Soc. 1998, 120, 6024 – 6036.* Al-MCM-41 is well known in the art and refers to an alumino-silicate known as the Mobil Composition of Matter described, for example, in WO-91/11390.

The ion exchange of the metal complex may be achieved in at least two different ways. In one method, a solution of a metal-ligand complex $[M(L)_n]^+[X]^-$ (where X is Cl, BF_4, OTf, or another suitable counter-ion) is stirred with the solid (H^+)-alumino-silicate with heating if required, followed by filtration and washing of the exchanged supported catalyst. The solvent is preferably a polar solvent, e.g. an alcoholic solvent such as methanol, ethanol or isopropanol. We have found that the use of a less-polar, non-protic solvent, e.g. dichloromethane, may result in incomplete exchange of the metal complex onto the support.

This preparation method may be illustrated by the example of the direct immobilisation of [Rh(R,R-Me-DuPHOS)(cod)][BF_4] , where cod is 1,5-cyclooctadiene, on Al-MCM-41 as follows:-



In a second method the supported catalyst is formed by first anchoring a cationic metal precursor onto the support by exchange with acid protons on the support and then adding the ligand to form the immobilised metal-ligand complex of the invention. A preferred example of a suitable cationic metal precursor is $[Rh(cod)_2][BF_4]$. The first step is simply achieved by stirring a solution of the cationic metal precursor (again preferably in a polar protic solvent such as methanol) with the support. The resulting immobilised cationic metal precursor may if desired be isolated before being treated with the ligand in a suitable solvent, e.g. methanol, acetone, tetrahydrofuran or dichloromethane to form the immobilised metal-ligand complex of the invention. An example of this method for the preparation of a [Rh(R,R)-Me-DuPHOS(cod)]Al-MCM supported catalyst is illustrated below.



This latter method may be preferable where the chiral ligand has a bulky structure that may reduce the ability of the cationic metal-ligand complex to enter the mesopores of the aluminosilicate support.

The invention further provides a process for performing a hydrogenation reaction comprising contacting a solution of the compound to be hydrogenated with hydrogen at elevated pressure in the presence of a solid catalyst comprising a chiral cationic metal-ligand complex immobilised upon a mesoporous alumino-silicate.

The solid catalysts of the present invention may be used for hydrogenation reactions. Preferred hydrogenation reactions are the hydrogenation of prochiral alkenes, chiral alkenes, ketones, imines and ketimines containing carbon-carbon double bonds and in

particular the hydrogenation of succinate, itaconate, methacrylate and acrylate esters, β-ketoesters, enol-acetates and enamides.

The reaction conditions for the hydrogenation reactions may be those well known to those skilled in the art but typically may be at temperatures in the range –10°C – 100°C and preferably 0 – 60°C, and at elevated hydrogen pressures in the range of 1 to 100 bar and preferably 3 to 30 bar. Pure hydrogen or hydrogen diluted with an inert gas may be used for the reactions. The amount of catalyst added to the reactions will depend upon the reaction conditions as well as the reactivity of the substrate (i.e. compound to be hydrogenated). Typically substrate : catalyst (metal) molar ratios of 100 – 5000:1 may be used in the present invention.

The invention is further illustrated by the following examples.

Example 1: The Preparation Of MCM-41 Type Mesoporous Aluminosilicates.
Al-MCM-41 type (Si:Al = 10:1)
A mixture consisting of tetramethylammonium hydroxide (101.21 g), cetyltrimethylammonium bromide (118.45 g), aluminium isopropoxide (26.56 g) and de-ionised water (860 ml) was stirred at 35°C for one hour. After this time fumed silica (78.0 g) was added and the resultant mixture was allowed to stir at room temperature for one hour. The gel was then transferred to an autoclave, purged with nitrogen gas (202.6 kPa) and allowed to heat to 150°C at 3°C per minute with slow stirring. The autoclave remained at the elevated temperature for a total of 48 hours. The contents of the autoclave were then cooled to ambient temperature (ca 20°C), filtered and washed with de-ionised water (1 litre) and ethanol (500 ml). The white solid was then oven-dried overnight (110°C for 16 hours) before being calcined under nitrogen at 550°C for 16 hours (ramp rate = 3°C per minute). After this, the solid was calcined for four hours in static air at 550°C.

Example 2: The Preparation Of SBA-15 Type Mesoporous Aluminosilicates (Si:Al 8:1).
Tetraethylorthosilicate (27 g) was mixed with aluminium isopropoxide (3.9 g) and aqueous hydrochloric acid (30 ml at pH = 1.5). This solution was stirred for three hours and then added to a second solution containing 12 g *poly*(ethylene glycol)-*poly*(propylene glycol)-*poly*(ethylene glycol) tri-block co-polymer with an average molecular weight of 5800 in aqueous hydrochloric acid (450 ml at pH = 1.5). The resultant mixture was stirred for one hour, charged to an autoclave and heated under nitrogen (202.6 kPa) with stirring to 100°C at 3°C per minute. The autoclave was held at this elevated spectrum for a total of 64 hours. The solid obtained was filtered, dried at 100°C overnight and calcined by heating in static air to 550°C at 25°C per hour and holding at the elevated temperature for 4 hours.

Example 3: Preparation of [Rh-(R,R-MeDuPHOS)(cod)]Al-MCM-41 by direct ion-exchange. A mixture of the solid support (H^+) Al-MCM-41, made in Example 1 (0.2 g) and [Rh-(R,R-MeDuPHOS)(cod)][BF_4] (0.020 g) in degassed methanol (5 ml) was heated at 55 °C for 1 hour during which time the solution became colourless and the solid took on a orange colour. The mixture was filtered and the yellow-orange solid washed with methanol (2 x 5 ml) and dried under vacuum. The yellow solid was stored under nitrogen.

Example 4A: Preparation of [$Rh(cod)_2$]Al-MCM-41.
A mixture of the solid support (H^+) Al-MCM-41 (Si:Al 10:1) (0.2 g) and [$Rh(cod)_2$][BF_4] (0.020 g, 0.05 mmol) in degassed methanol (5 ml) was stirred at 50 °C overnight under a nitrogen atmosphere. The solid material took on a pale orange colour. The following day the liquid was decanted and a further portion of methanol added. The mixture was filtered and the solid dried under vacuum.

Example 4B: Preparation of [Rh-(R,R-MeDuPHOS)(cod)]Al-MCM-41.
A mixture of [$Rh(cod)_2$]Al-MCM-41 (0.176 mg) as prepared in Example 4A and (R,R)-MeDUPHOS (16 mg, 0.05 mmol) in degassed methanol (5 ml) was stirred at 50°C for 1.5 hours. The solid material changed from a pale orange solid to a yellow colour, whilst the methanol solution also became a pale yellow colour. The mixture was cooled to room temperature (ca 20°C) and then filtered. The yellow solid was then washed thoroughly with methanol and dried under vacuum.

Example 5: Hydrogenation of dimethyl itaconate.
Dimethyl itaconate (about 1 mmol) and catalyst were weighed into a glass-liner that was placed inside a 50ml autoclave to give a substrate:catalyst (Rh) molar ratio of 1000:1. The autoclave was sealed and flushed with nitrogen. The autoclave was then pressurised with hydrogen to 80 psi (506.6 kPa) and then released (cycle repeated 5 times). Sufficient methanol was added to the autoclave to give an approximately 1M solution of substrate and the 5 cycles of pressurising-releasing with hydrogen were repeated. Finally the autoclave was pressurised with H_2 to 80 psi (506.6 kPa), sealed and left to stir. After the desired time the stirring was stopped and the H_2 released slowly. The autoclave was flushed with nitrogen and the liquid phase removed by syringe through a valve (SWAGELOK™) opening. The products were analysed by chiral gas chromatography using a LIPODEX-E™ column. The conversion after 1 hour and the enantiomeric excess (ee) are shown in Table 1 for different [Rh(Ligand)(cod)]Al-MCM-41 (cod = 1,5-cyclooctadiene) complexes immobilised using the method of Example 3.

Table 1

Ligand	Conversion (%)	ee (%)
(*R*)-BINAP	82	43
(*R*)-PROPHOS	34	31
(*R,R*)MeDUPHOS	99	98

Example 6: Re-use of supported catalyst.

The hydrogenation procedure of Example 5 was repeated using the catalyst [Rh(R,R-Me-DuPHOS)(cod)]Al-MCM-41 immobilised according to the method of Example 3 at a substrate : catalyst (Rh) molar ratio of 250:1. After 1 hour (unless otherwise stated) the solid was allowed to settle and the liquid phase was removed by syringe under a positive flow of nitrogen. A fresh aliquot of substrate in methanol (at the same substrate : catalyst ratio) was then added to the autoclave which was re-pressurised with H_2. Conversion and enantiomeric excess (ee) were determined as after each run. The results are shown in Table 2.

Table 2

Run	Conversion (%)	ee (%)
1	> 99	> 99
2	> 99	> 99
3	> 99	> 99
4	> 99	> 99
5	99	98
6	98	96
7	95	95
8	99	95
9 (overnight)	93	94

The results show that the solid supported catalyst may be successfully reused many times whilst maintaining its catalytic activity.

Example 7: Comparison with homogeneous catalyst.

The hydrogenation of dimethyl itaconate was performed using the general procedure of Example 5 in methanol (1 M) at 20°C with a substrate : catalyst (Rh) molar ratio of 5000:1 and at 506.6 kPa H_2 using the immobilised catalyst [Rh(R,R-MeDuPHOS)(cod)]Al-MCM-41 (cod = 1,5-cyclooctadiene), prepared according to Examples 4A/4B (i.e. via the cationic precursor complex $[Rh(cod)_2][BF_4]$). After the time shown in Table 3, the solid was allowed to settle and the liquid phase was removed by syringe under a positive flow of nitrogen. A fresh aliquot of substrate (at the same substrate : catalyst ratio) in methanol was then

added to the autoclave, which was re-pressurised with H_2. Conversion and enantiomeric excess (ee) were determined as before after each run.

As a comparison, the reaction was performed in methanol (1 M) at 20°C, with a substrate : catalyst ratio of 5000:1 and at 506.6 kPa H_2 using the unsupported homogeneous catalyst [Rh(R,R-MeDuPHOS)(cod)][BF_4] following the general procedure of Example 5. The results are shown in Table 3.

Table 3

Run	Time (h)	Conversion (%)	ee (%)
1	1	> 99	96
2	2.5	98	97
3	12	97.5	94
Homogeneous catalyst (comparison)	1	> 99	94

The results demonstrate that even at high substrate:catalyst ratios, the supported catalyst produces results which are at least comparable to the corresponding homogeneous metal –ligand catalyst complex.

Example 8: Hydrogenation of dimethyl itaconate using SBA-type supported ligands.

Two [Rh-(R,R)-MeDuPHOS(cod)]SBA-15 catalysts were prepared using the general methods described in Examples 3 and 4A/4B, using the (H^+)-SBA-15 prepared in Example 2, and either [Rh-(R,R)-MeDuPHOS(cod)][BF_4] or [Rh(cod)$_2$][BF_4] and (R,R)-MeDuPHOS respectively. The catalysts were tested in the hydrogenation of dimethyl itaconate according to the general method of Example 5 (with a substrate : catalyst (Rh) molar ratio = 1000:1). Conversion of the substrate was complete after 15 minutes giving a product having in each case, an enantiomeric excess of 98%.

Example 9: Hydrogenation of methyl-2-acetamidoacrylate using SBA-type supported ligands.

A [Rh-(R,R)-MeDuPHOS(cod)]SBA-15 catalyst prepared according to the method of Example 3 was used for the hydrogenation of methyl-2-acetamidoacrylate (MAA) according to the general method of example 5 (using about 1 mmol MAA and a substrate : catalyst (Rh) molar ratio = 1000:1) and then re-used several times at the same substrate: catalyst ratio according to the basic method as used in Example 6. The reaction scheme and results are shown below and in Table 4.

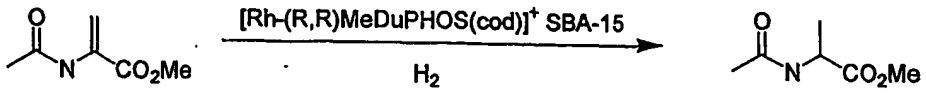


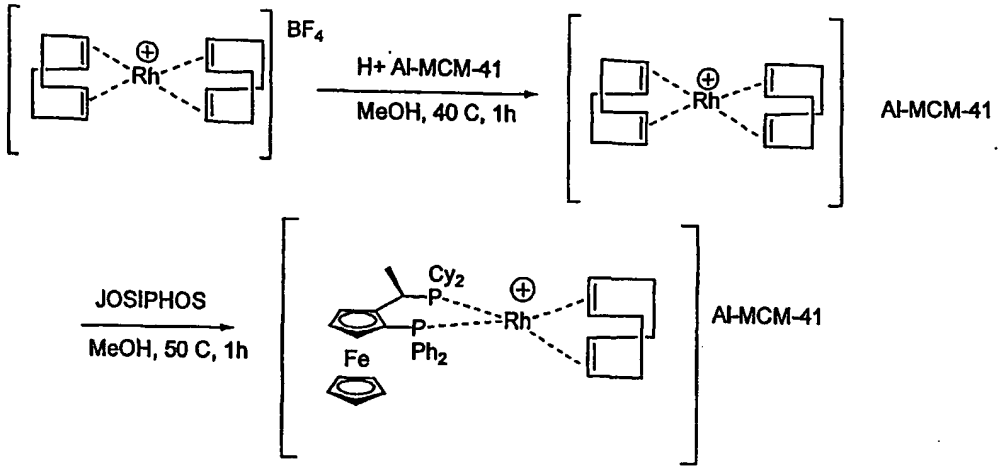
Table 4

Run	Time to full conversion	ee (%)
1	10	95
2	10	99
3	10	97
4	15	97
5	20	92
6	30	80
7	45	79

The results show that the catalysts can be isolated and re-used many times whilst maintaining high activity.

Example 10A: Preparation of $[Rh(cod)_2]$Al-MCM-41 having a higher Si:Al ratio.
A mixture of a lower Al-containing solid support H^+ Al-MCM-41 (Si:Al = 73:1) (0.73 g) and $[Rh(cod)_2][BF_4]$ (0.010 g, 0.024 mmol) in degassed methanol (10 ml) was stirred at 40 °C for 1 hour under a nitrogen atmosphere. The solid material took on a pale orange colour. The liquid was decanted and a further portion of methanol added. The mixture was filtered and the solid dried under vacuum.

Example 10B: Preparation of [Rh-(R,S-JOSIPHOS)(cod)]Al-MCM-41.
The $[Rh(cod)_2]$Al-MCM-41 (0.7 g) as prepared in Example 10A and (R,S)-JOSIPHOS (15.3 mg, 0.024 mmol) in degassed methanol (10 ml) was stirred at 50°C for 1 hour. The solid material changed from a pale orange solid to a yellow colour, whilst the methanol solution also became a pale yellow colour. The mixture was cooled to RT and then filtered. The yellow solid was then washed thoroughly with methanol and dried under vacuum. The preparation of the catalyst is depicted below.



Example 11: Hydrogenation reaction using [Rh-(R,S-JOSIPHOS)(cod)]Al-MCM-41. Dimethyl itaconate was hydrogenated following the general method described in Example 5 using a substrate : catalyst (Rh) molar ratio of 500:1, but allowing only 15 minutes reaction time. The catalyst was allowed to settle and the supernatant containing the product removed by syringe. The catalyst was then re-used (at the same substrate : catalyst ratio) according to the method of Example 6. The results are given in Table 5.

Table 5

Run	Conversion (%)	ee (%)
1	99	94
2	99	92
3	99	92
4	99	92
5	99	91
6	98	91
7	98	91
8	99	92
9	98	91
10	98	90

The results show that the JOSIPHOS catalyst may be successfully immobilised on a mesoporous support having a higher Si:Al ratio and that the resulting catalyst is active and selective, and may be recycled without significant reduction in activity or selectivity.

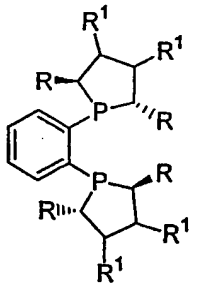
Claims

1. A solid catalyst for asymmetric hydrogenation reactions comprising a chiral cationic metal-ligand complex immobilised on a mesoporous alumino-silicate support.

2. A catalyst as claimed in claim 1 wherein the cationic metal-ligand complex is represented by the formula $[M(L)_n]^+$, in which;
M is a metal ion which may be selected from Rh^{1+}, Ir^{1+} or Ru^{2+},
L is a neutral mono- or bidentate ligand and n is 1 or 2.

3. A catalyst according to claim 1 or claim 2 wherein the catalyst further comprises at least one further stabilising ligand such as a diene, alkene, carbonyl or aryl group.

4. A catalyst as claimed in claim 2 or claim 3 wherein the neutral ligand is selected from the group consisting of BINAP, DuPHOS, BIPHEP, TMBTP, BITIANAP, BIBFUP, bppm, CARBOPHOS, JOSIPHOS, BPE, DEGPHOS, DIOP, BIPNOR, DIPAMP, CHIRAPHOS, PROPHOS, PYPHOS, BINAPAN, SELKE or



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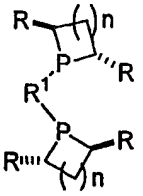

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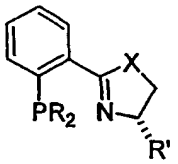

R= H, alkyl, alkoxy, hydroxy, amino, aryl
R^1 = H, hydroxy, alkoxy, amino

R^1 = alkyl, aryl, ferrocenyl, ruthenocyl,
n = 0, 1, 2, 3 etc
R = alkyl, alkoxy, hydroxy, amino, aryl

R' = alkyl, phenyl,
R = aryl, alkyl, alkoxy, amino
X = O, S, N

5. A catalyst according to any one of claims 1 to 5 wherein the cationic metal-ligand complex is $[(R,R)$-MeDuPHOS-Rh(1,5-cyclooctadiene)$]^+$ or $[(R,S)$-JOSIPHOS)Rh(I)(1,5-cyclooctadiene$)]^+$.

6. A catalyst according to any one of claims 1 to 5 wherein the support is a mesoporous silicate material having acidic sites suitable for ion exchange provided by aluminium and having a Si:Al ratio in the range 4 – 500 : 1 by weight.

7. A catalyst according to any one of claims 1 to 6 wherein the support is SBA-15 or Al-MCM-41

8. A method of forming a solid catalyst comprising a chiral cationic metal-ligand complex immobilised on a mesoporous alumino-silicate support, comprising the steps of:
   a) forming a solution of a metal-ligand complex $[M(L)_n]^+[X]^-$ where X is Cl, BF_4, OTf, or another counter-ion in a polar solvent,
   b) stirring together said solution with a solid support comprising a mesoporous aluminosilicate,
   c) filtering the resulting solid from the supernatant liquor, and
   d) washing the catalyst with solvent.

9. A method of forming a solid catalyst comprising a chiral cationic metal-ligand complex immobilised on a mesoporous alumino-silicate support, comprising the steps of:
   a) forming a solution of a cationic metal precursor in a polar solvent
   b) stirring together said solution with a solid support comprising a mesoporous aluminosilicate
   c) filtering the resulting solid from the supernatant liquor
   d) stirring together said solid with a solution of a neutral ligand in a solvent, and
   e) filtering the resulting solid from the supernatant liquor.

10. A method according to claim 9 wherein the cationic metal precursor is $[Rh(cod)_2][BF_4]$.

11. A method according to any one of claims 8 to 10 wherein the polar solvent is methanol.

12. A process for performing a hydrogenation reaction comprising contacting a solution of the compound to be hydrogenated with hydrogen at elevated pressure in the presence of a solid catalyst comprising a chiral cationic metal-ligand complex immobilised upon a mesoporous alumino-silicate.

13. A process according to claim 12 wherein the compound to be hydrogenated is selected from the list comprising a prochiral alkene, chiral alkene, ketone, imine or ketimine.

14. A process according to claim 12 or claim 13, further comprising the step of separating the solid catalyst from the reaction mixture, and using it in a subsequent hydrogenation reaction.

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